Tampere University

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NANOCELLULOSE FILM FABRICATION
Stability and Challenges

Faculty of Information Technology and Communication Sciences
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ABSTRACT

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Being the main substance of the walls of plant cells, cellulose is the most common organic polymer on earth. Plants produce about 180 billion tonnes of cellulose annually. This makes cellulose an almost inexhaustible raw material, which in turn makes it an interesting and renewable film material for applications in different areas. In recent years, nanocellulose has indeed gained more interest as a prospective fabrication material in various fields.

While cellulose-based materials, such as cotton in textiles and wood as building materials, have been known to humankind for centuries upon centuries, nanocellulose is still a fairly young material when it comes to mainstream usage and production. Its roots span to the 1980s, when microfibrillated cellulose was first introduced to the public. Since then, nanocellulose's great mechanical, optical and electrical properties as well as its optimal surface modification possibilities have garnered more interest and research in its direction. New processing methods to procure nanocellulose have been discovered, while faster and more efficient film fabrication methods have been developed. However, problems with expensive and slow methods still hinder the progress of nanocellulose-based films.

This paper discusses nanocellulose as a viable material for film fabrication. In this paper, the advantages and disadvantages of different nanocellulose types and film fabrication methods used to produce cellulose-based film applications are described and compared. It can be stated that different methods require different approaches, such as choosing suitable nanocellulose materials and fabrication methods needed for specific applications. Nanocellulose can be described as a material of many opportunities and it offers new solutions to old problems that arise with unsuitable and nonrenewable film materials.

Keywords: nanocellulose, cellulose, renewability, film technology, film fabrication, nanocellulose films

CONTENTS

1. INTRODUCTION

Annually, plants produce about 180 billion tonnes of cellulose. This makes cellulose the most common organic polymer on earth. [1] It was first studied and extracted in 1838 by a French chemist Anselme Paven, who discovered 'a resistant fibrous solid substance' when plant tissues were treated with acids and ammonia and then with a mixture of water, alcohol and ether [2]. In addition, he discovered the presence of cellulose in cotton, which is one of the most widely used natural fibres in the world, with nearly 90% of its fibres being cellulose [2][3].

Nanocellulose refers to nano-structured cellulose and its properties differ vastly from those of traditional cellulose. A type of nanocellulose was first introduced to the public by Turbak, Snyder and Sandberg in 1983 in their paper *"Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential"* [4]. Since then, the interest towards nanocellulose as a material has only grown due to its unique properties [5][6][7].

Because of nanocellulose's unique properties, nanocellulose films have the potential for transparency and extreme strength [8]. Nanocellulose is also biocompatible, making it an eligible candidate for biomedical and tissue engineering solutions. In addition, nanocellulose is an attractive material for sensor technology and printed electronics, because of its conductive and piezoelectric properties.

Recently, there has been a rise in interest concerning renewability and ecological living and production. Nanocellulose, as a completely natural polymer, is renewable, abundant and recyclable, thus making it a hot topic as a potential material for sustainable fabrication. These aforementioned properties make nanocellulose an interesting substance to study, which is why this paper is dedicated to reviewing existing studies on nanocellulose films. The purpose of this paper is to study the properties of cellulose and nanocellulose, as well as to consider the eligibility of them as film fabrication materials. Different film fabrication methods will in addition be reviewed. A special interest for this paper will be the fabrication methods discussed in a study by Pammo et al., *"Nanocellulose films as substrates for printed electronics"* [9]. In addition, different application areas will be discussed.

The properties, structure and main characteristics of cellulose will be discussed in the following chapter. In chapter 3, fabrication methods for nanocellulose films are presented. Chapter 4 combines the topics of chapter 2 and chapter 3, and the properties of nanocellulose films will be discussed specifically. Results will be gathered into a table for easy viewing. Chapter 5 concludes this paper, presenting the main thoughts raised during the writing of this paper.

2. CELLULOSE AS A MATERIAL

By the *Oxford Dictionary of English*, the word 'material' is defined as 'the matter from which a thing is or can be made' [10]. Different materials have different properties, and they can be classified into different groups by these properties, their compositions, molecular structures, usages and so on. The typical classification of materials is into four different groups, which are metals, ceramics, polymers and composites.

Cellulosic materials fall into the category of organic polymers. In the following chapters, usages, sources, structure and properties of cellulose are discussed.

2.1 Usages and Sources of Cellulose

Cellulose is the main substance of plant cells' walls and is thus found abundantly in nature. Of the annual global biomass production, cellulose, with 1.5×10^{12} tons, is the most common of the organic polymers and considered almost inexhaustible as a raw material [11].

Depending on how it is processed, cellulose can be used in different fields for various applications. Traditional uses of cellulose include paper, textiles and building materials. As Egyptian papyri, cellulose also has had extensive cultural importance as a means of record and transmission [12]. Cellulose has also had an important role as fiber in human diet, ensuring the proper working of the intestinal tract as bulk. As a chemical raw material, the use of cellulose spans for around 150 years [12].

More recent applications of cellulose include different films, coatings, membranes and plies. Cellulose has also been used as a reinforcement material in composite materials, typically with hydrophobic polymers [13]. Different biomedical and electronic applications based on cellulosic materials have emerged in recent years as well, with the potential of replacing traditional component materials with cellulose-based materials in these fields. The possibilities for different application areas are vast.

As stated previously, cellulose is the most common organic polymer on the earth, and it is easily found in nature. Some of the most important sources of cellulose are plants, animals, algae, fungi and minerals. The most notable of these sources is plant fiber, since cellulose attributes around 40% of carbon fraction in them. [13] Important sources of plant fiber include wood, bamboo, cotton and flax.

Other than plant fibers, cellulose can also be obtained from certain bacteria, algae and fungi, as well as some sea creatures (tunicates) [11][13]. Because cellulose derived from these sources possesses specific supramolecular structures, these fibers are typically utilized for research on structure, crystallinity, and reactivity of cellulose. These celluloses can also be used for the benefit of developing new materials and biomaterials. [11]

In addition to natural sources where cellulose is formed by photosynthesis, cellulose has also been chemically synthesized. The first chemical synthesis of cellulose was accomplished by enzymatic polymerization, which is a polymer synthesis method developed for the very purpose [14]. However, in terms of time, work intensity or the properties of the cellulose products, methods of chemical synthesis are not yet completely satisfactory [13].

Regenerated cellulose fibers are natural fibers that have been extracted from their source by the use of a solvent. Especially for mass production, for example in the textile industry, regenerated cellulose fibers are the only ones directly sourced from a natural polymer which is renewable, abundant and biodegradable. Regenerated cellulose fibers also possess different properties than natural fibers, such as homogeneity and the adjustability in the processing. [15] Regenerated cellulose can be used to manufacture fibers, films, membranes and sponges [11].

Cellulose has also been studied as an applicable nanocomposite material. Characteristics such as good mechanical properties and conductive nanocomposite networks offer new application areas, for example in sensors or interference shielding [16]. However, while cellulose seems to be an attractive option for nanocomposite reinforcing agents, problems with processing still need to be overcome before efficient production [12].

2.2 Properties and Characteristics of Cellulose

Cellulose exhibits many interesting properties that could be harnessed in favor of different applications. However, to efficiently utilize cellulose as a material, these properties and where they originate from must first be understood. In the following chapters the structure, properties, processing methods and morphology of cellulose are discussed. In addition, the main differences between cellulose and nanocellulose will be presented.

2.2.1 Structure of Cellulose

Cellulose is a linear polymer, composed of a repeating unit known as cellobiose, which is a six-membered ring that contains an oxygen atom and three OH groups, joined by an oxygen atom [5][17]. These units are linked to each other by β-1,4-glycosidic bonds. It has a ribbon-like conformation with every one of its unit oriented at 180 degrees. Because of this linearity, hydrogen bonding between adjacent chains is typical, leading to the formation of fibers [17]. The molecular composition of cellulose is depicted in Figure 1, where we can see that cellulose is chiral.

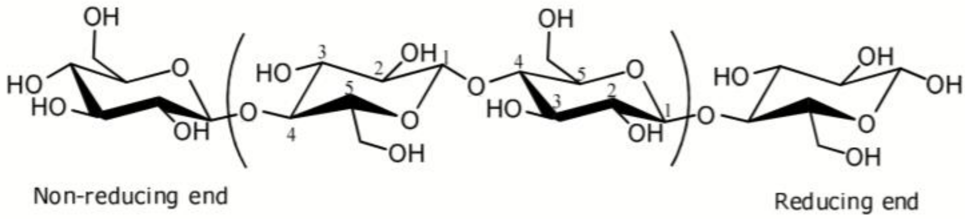

Figure 1. *The structure of a cellulose molecule. [5]*

The chemical formula of cellulose is $(C_6H_{10}O_5)_n$. In the formula n expresses the number of glucose units in a polymer molecule, in other words the length of the polymer chain, or the degree of polymerization (DP). These properties depend on the source of the cellulose and the method used to isolate cellulose from its plant source [5].

Cellulose is tasteless, odorless, hydrophilic, and insoluble in water and in most other organic solvents. Because of their long chains that prevent efficient packing in a crystal lattice, linear polymers do not form crystalline solids. This is why cellulose consists of both crystalline as well as amorphous regions, where tightly packed crystalline regions give toughness to it and amorphous regions give flexibility.

Cellulose can be hydrolyzed to glucose by severing the β-glycosidic bonds. Inside cells, this is achieved by an enzyme known as β-glucosidase. Humans cannot digest glucose because the human body does not contain this enzyme. [17] However, as mentioned in chapter 2.1, cellulose can still be ingested, and it is an important fiber as a part of human diet.

As stated previously, the hydrogen bonding between cellulose units is typical. Because of this, an intramolecular and intermolecular hydrogen bond network is formed between OH groups on the glucose units, either within the same chain or between different chains [5]. Intramolecular hydrogen bonds maintain stability and provide strength in the chain in the cellulose conformation. Interchain cohesion and packing is controlled by the intermolecular hydrogen bonds. Intermolecular bonds also enable the strong interaction between cellulose chains [13].

Many of cellulose's properties, such as limited solubility in most solvents, reactivity of the OH groups and its crystallinity, can be attributed to these strong hydrogen bonds [13]. They also enhance the mechanical properties of cellulosic materials [16]. The mechanical properties and crystallinity of cellulose will be discussed in the following chapter.

2.2.2 Mechanical Properties and Crystallinity

Because of the structure of the fibrous structure of cellulose, many species of plants found in nature have unique strength and high-performance properties. It can be argued that the most important properties of lignocellulosic materials, such as wood, are their mechanical properties. These materials possess high mechanical strength and high strength-to-weight ratio, but still remain flexible. [18]

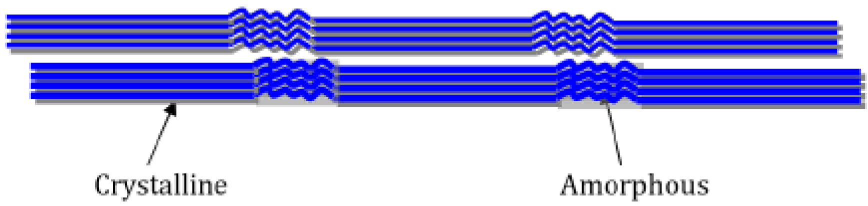

Figure 2. *Crystalline and amorphous regions in cellulose microfibril. [5]*

Many of cellulose's mechanical properties originate from the interactions between its crystalline and amorphous regions, as well as from the regions and their properties themselves. Because of these regions, cellulose is a highly mechanically heterogeneous material. The amorphous regions provide flexibility and plasticity, while the crystalline regions provide strength and rigidity. [19] The crystalline and amorphous regions in a cellulose microfibril are depicted in Figure 2.

Cellulose has four different crystalline forms (allomorphs), one in its native form while the other three forms are achievable through different treatments. These different allomorphs show different degrees of reactivity, strength and different hydrogen boding [13]. The crystallinity of these forms can be measured by using X-ray diffraction or solid-state nuclear magnetic resonance (ssNMR) spectroscopy.

Because of the crystallinity of cellulose, properties like piezoelectricity are attainable. Piezoelectric materials accumulate charge under applied mechanical stress, and they are widely utilized in applications like sensor and actuator technologies. Cellulose offers properties like flexibility, transparency and biocompatibility, which are not found in many of the traditional piezoelectric application materials. [20]

2.3 Cellulose Processing

Cellulose can be derived from natural or man-made regenerated fibers. Typical sources of cellulose were discussed in chapter 2.1. The most notable of these sources is plant fiber. Wood contains approximately 40% cellulose, and as a form of wood pulp, it remains a major source of cellulose, taking up around 90% of global pulp production [5]. Wood pulp is the most important raw material source for the processing of cellulose [11].

With the exception of cotton, which naturally occurs as nearly pure fibers, cellulose primarily exists as part of lignocellulosic material or semipure fibers. Plants that consist of cellulose, hemicellulose and lignin are lignocellulosic materials. When cellulose is derived from sources such as these, it needs to be isolated through pulping. This removes lignin, hemicellulose and other substances that are not desirable in the final product, such as pectins, waxes, minerals and proteins. [5] Different methods have been developed for this isolation, which will be discussed in this chapter.

Because of cellulose's hydrogen bonding, which was discussed in greater detail in chapter 2.2, cellulose is difficult to process as a melt or solution [15]. Alternative processing methods are therefore needed.

Regenerated cellulose is usually processed by either chemical derivatization or direct physical dissolution in a solvent. The viscose process is currently the most important large-scale method of producing cellulose fibers and films [11][15]. With this method, viscose is regenerated by having cellulose react with sodium hydroxide and carbon disulfide. However, with the use of large amounts of these reactants, hazardous by-products, such as gaseous hydrogen sulfide, are formed, causing potential harm to the environment [13].

A more environmentally friendly cellulose processing method to the viscose process was developed a little more than 100 years after the viscose process, when in 1989 the name Lyocell was given for solvent-spun fibers [11][13]. This method utilizes a direct solvent, N-methylmorpholine-N-oxide (NMMO), from where cellulose is regenerated by spinning [11][15]. Methods with the use of direct solvent such as the Lyocell method, have shown great potential in shaping cellulose and producing functional celluloses [15].

2.4 Nanocellulose

Particles with at least one dimension between 1–100 nm are referred to as nanoparticles. The properties at this scale differ from those at macroscale, mainly the DP, and depending on the processing method, the crystallinity and shape of cellulose being affected [13]. With cellulose, the nanodimensions of the structural elements create a high surface area. This leads to powerful interactions between cellulose and surrounding substances, such as water, compounds, other nanoparticles and living cells. [12] Other properties of nanocellulose include high mechanical strength, interesting optical and rheological properties, as well as easier surface modification [5].

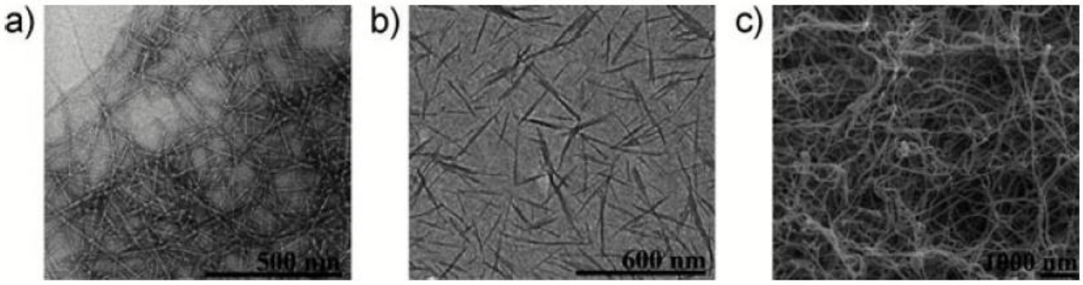

Figure 3. *The three nanocellulose types a) MFC, b) CNC and c) BNC. [12]*

Nanocellulose is generally divided into three different types. These types are cellulose nanocrystals, microfibrillated cellulose and bacterial nanocellulose, which are pictured in Figure 3 above. [5][12] The preparation methods for these nanocellulose types are different and will be discussed in the following chapters.

2.4.1 Cellulose Nanocrystals

Cellulose nanocrystals (CNC) are stiff rod-like particles with the average diameter of 5–70 nm and its length ranging between 100–250 nm when it has been extracted from plant cellulose, and from 100 nm to several micrometers when it has been extracted from tunicates, algae or bacteria [12]. They are sometimes referred to as whiskers, nanocrystalline cellulose, crystallites and so on.

CNC is generated by the release of crystalline regions from the semicrystalline cellulosic fibers by hydrolysis with mineral acids [12]. Thus, CNC is typically prepared by an acid hydrolysis of pure cellulose, usually utilizing inorganic acids [5], followed by ultrasonic treatment [12]. Because of the tight packing of crystalline regions, amorphous regions are hydrolyzed more efficiently than crystalline ones and CNCs are formed [5]. This leads to CNC consisting of the extracted crystalline regions of cellulose, positioned in a nearly perfect crystalline structure.

However, correct timing of the hydrolysis remains essential. If hydrolysis time is insufficient, amorphous regions of cellulose might remain in the product, resulting in the reduction of crystallinity and change in particle morphology. On the other hand, if the hydrolysis time stretches too long, depolymerization of crystalline cellulose may occur, decreasing the aspect ratio of the nanocrystals. [21]

Major sources of CNC include wood, cotton, hemp and flax. Depending on the source of the cellulose and their degree of crystallinity, the dimensions and geometries of extracted nanocrystals vary. [12]

CNC is one of the strongest and stiffest natural biopolymers, making it an appropriate candidate for the tailoring of mechanical properties of polymer materials [22]. CNC is dispersible and has low susceptibility to bulk moisture absorption, as well as large surface area. This makes CNC a potentially attractive reinforcement material for composites. [12]

2.4.2 Microfibrillated Cellulose

Microfibrillated cellulose (MFC) was first developed by Turbak, Snyder and Sandberg in 1983. MFC was the first form of nanocellulose to be discovered, and Turbak et al. introduced it in their paper "*Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential".* They had found that a new, gel-like form of cellulose could be produced by a unique physical treatment of wood pulp. [4]

MFC is prepared by mechanical disintegration. High shear forces, where wood-based cellulose fibers are forced through mechanical devices, combined with either chemical or enzymatic pre-treatment, are applied in the preparation. [5][12] This treatment delaminates the fibers, extracting the microfibrils [12].

The microfibrils that form MFC are highly entangled and connected, forming mechanically strong networks and gels. The interactions between fibrils cause much stronger gels than those formed by hydrogen bonds between just water and fibrils. [13] The average diameter of a microfibril is between 5–60 nm and its length is typically several micrometers [12]. Other names for MFC include cellulose nanofibrils, microfibrils and nanofibrillated cellulose.

Notable sources of MFC are wood, sugar beet, hemp and flax [12]. MFC has high specific stiffness and strength that depend on its crystallinity. It is biocompatible and steadily becoming more affordable. [23] In addition to traditional MFC materials, MFC can also be used to prepare aerogels and foams, materials which offer new application possibilities.

2.4.3 Bacterial Nanocellulose

Unlike CNC and MFC, which are prepared using top-down approaches, bacterial nanocellulose (BNC) is prepared via bottom-up approach. This includes the use of cellulose producing bacteria. [5] BNC is synthesized as a protective envelope around cells, forming a pellicle-shaped hydrogel when cultured under static conditions [24].

The typical diameter of BNC is 20–100 nm, forming different types of nanofiber networks. Other names for BNC include bacterial cellulose, microbial cellulose and biocellulose. [12]

BNC contains no lignin or heteropolysaccharides, unlike cellulose from plant sources [6]. This leads to high purity. In addition, BNC has great tensile strength, hydrophilicity, high crystallinity and biocompatibility [24], as well as stable mechanical properties [12].

Sources of BNC include sugars and alcohols with low molecular weight, where fermentation can occur. BNC is formed from these sources as a result of a biotechnological assembly process. [12] Some aerobic bacterial strains, such as *Gluconacetobacter xylinus*, nowadays known as *Komagataeibacter xylinus*, can produce cellulose via bacterial synthesis. [12][20]

BNC can be cultivated under static conditions on an appropriate medium. The process of obtaining BNC and BNC-based films will be discussed in more detail in chapter 3.2.1.

3. FILM FABRICATION

Films are a type of technology used broadly in various fields. They consist of a layer of material, the thickness of which varies, but which is typically between 10 nm – 50 µm.

Films can be categorized into thin-films and thick-films. When it comes to nanocellulose films, the films are typically divided into coatings and free-standing films. The general ideas of film technology, different film fabrication methods and usages of film technology will be presented in the following chapters.

3.1 Film Technology

Regarding cellulose-based materials, films are typically divided into two categories: thin-films, fabricated by placing them onto a substrate, known as coatings, and thick-films, known as free-standing films, which are fabricated to stand freely by themselves. These films require different fabrication methods, which result in different properties of the films.

Polymer thin-film technology has advanced in recent years, providing better barrier and optical properties, wear resistance and so on. Because of this, the demand for polymeric thin-films has increased with applications ranging from traditional industries like paper to automotive industry to packaging and electronics. [25] New, sustainable and renewable materials are needed to replace traditional materials for films.

Nanocellulose has proved its potential application areas in numerous technical fields [26]. Since nanocellulose is a renewable, organic polymer with unique properties, which described earlier in this paper, films fabricated from it can be processed to obtain innumerable combinations of different properties.

Many of these properties are dependent on the fabrication method. In the following chapters common film fabrication methods for nanocellulose-based materials will be presented.

3.2 Film Fabrication Methods

A traditional film fabrication method is by deposition [27], but depending on the desired thickness, properties and material of the film, different approaches to fabrication are needed. For instance, different fabrication methods are appropriate for coatings and free-standing films.

Four most widely used nanocellulose film fabrication methods, particularly for thin films, are casting, coating, papermaking and extrusion. [6] Usually, films are prepared either by vacuum filtration or casting. In vacuum filtration fiber suspensions are filtered via mesh filter where fibers can form a film, whereas in casting the fiber suspensions are poured onto a surface for drying. [28]

As for thin film preparation, the sparse solubility of cellulose is one problem, since unlike films based on inorganic materials that are typically fabricated using vapor deposition techniques, soft materials usually require solution-based techniques. [29] Approaches for nanocellulose coatings include rod-coating, sheet forming and layer-by-layer deposition. [30]

Films for specific functions can also require processing after fabrication. Films can be patterned via lithography [29], while some films require polishing [31]. For different methods and results, different steps need to be taken.

In the following segments, the most commonly used nanocellulose film fabrication methods are introduced. In addition, some relevant studies on different films are described. The methods are listed in an alphabetical order.

3.2.1 Biofabrication

The fabrication methods concerning BNC are unique to the material, which is why these methods will be discussed in their own chapter. The properties and common sources of BNC were presented earlier in chapter 2.4.3.

Biofabrication can be defined as the manufacturing of biologic products from materials such as cells, proteins, molecules and other biological materials. In this context, biofabrication will be used to refer to the production of nanocellulose films from BNC.

For BNC film biofabrication, certain materials are required, such as a strain of bacteria able to produce cellulose, composite partners, typically organic compounds, as well as an appropriate culture medium [12][32]. Bacterial cells are usually pre-cultivated, before transferring them onto the medium [20].

On the medium, BNC films need to be cultivated for several days, the exact time depending on the strain of bacteria and cultivation conditions. A continuous supply of oxygen and static conditions are needed for cultivation [12][20]. Room temperature or some degrees above is usually appropriate for effective cultivation. After the cultivation period, BNC films can be collected. Non-cellulose materials are removed, for instance by immersion into potassium hydroxide solution [32]. Following the immersion, the BNC films are rinsed and washed.

BNC films consist of cellulose chains that combine into fibrils, forming a nanofiber network [12]. BNC membranes have been used for countless applications because of their unique properties and sustainable and cost-efficient production methods. While issues with tight pore structures have been discovered, by choosing correct carbon sources the morphology of BNC can be altered according to need. [32]

The good biocompatibility of BNC-based materials has also been demonstrated. In one study, BNC-based vascular grafts were implanted into animals with results that indicated good biocompatibility of BNC and its incorporation in the body. [12]

3.2.2 Dip Coating

In the dip coating process, the substrate is immersed in a liquid for deposition and then lifted out of the solution at a preset speed. Cellulose-based films produced by dip coating were studied in a 2016 paper by Herrera et al [30].

Nanocellulose films fabricated by dip coating are thin coatings, typically prepared by using layer-by-layer assembly. By dip coating method, anisotropic coatings can be manufactured on top of substrates. The thinness of the coatings is easily controllable by altering the concentration of the suspension used. [30]

By dip coating, nanocellulose layers with high oxygen barrier at low humidity could be produced. However, after multiple layers delamination may become an issue from substrates with small pores. In addition, the coatings produced were sensitive to prolonged storage and humidity. [30]

Dip coating can in addition be utilized after vacuum filtering, where multilayered anisotropic membranes have been produced from CNC. The thin films were dip coated by a dispersion of CNC with sulfate or carboxyl surface groups. Membranes with small pore size could be produced with this method. [33]

3.2.3 Electrospinning

Electrospinning is used often for the fabrication of fibrous films. An electric field is used to deform polymer solutions into fibers by charging them and depositing them on a collector. Equipment such as high-voltage source, syringe pump, metal needle tip and a collector are needed.

Nanofiber films are most commonly fabricated using electrospinning. In the electrospinning process, polymer solutions or melts are ejected into unstable jets by the use of high voltages. The jets reduce in size, forming long nanoscale fibers, typically ranging from hundreds of nanometers to a few micrometers in length. [34] Electrospun nanofiber films have been shown to possess porous structures and high specific surface areas [35].

When it comes to electrospinning cellulosic materials, challenges have arisen because cellulose does not melt and is difficult to dissolve into a homogeneous solution. However, as mentioned in chapter 2.3 cellulose can be dissolved using NMMO, but also using lithium chloride/dimethyl acetamide (LiCl/DMAc) and ionic liquids. Electrospinning cellulose into fibers from these solvents induces various dielectric and solvent removal constraints. These solvents require specific conditions for film production and are not feasible for continuous fiber production. [34]

An aqueous solvent for cellulose, NaOH/12, was created in 2010. With this solvent, cellulose with relatively low molecular weight was electrospun successfully into fibers. In addition, pure cellulose solution was electrospun into particles with diameter ranging between 100-300 nm rather than fibrous materials. With further research, ultra-thin fibers could be produced for biomedical and bioengineering applications. [36] Cellulose derivatives such as hydroxypropyl cellulose, hydroxypropyl methyl cellulose and ethyl-cyanoethyl cellulose can also be dissolved in solvents that can be electrospun. [34]

3.2.4 Foam Forming

Foams are multiphase systems. They can be either solid or liquid, typically with a high amount of gas pockets, which makes foam a light-weight material. Liquid and solid foams can be used for different kinds of applications and are categorized differently. [37]

Because of foam’s unique rheological characteristics and high surface area, it can be utilized in several industrial processes, for instance wastewater treatment, recycled paper deinking, in the food industry as well as in oil recovery. [37] Foam forming could also be used to save raw material, especially in packaging applications. [38]

With foam forming, it is possible to fabricate products with consistent properties and excellent formation. Foam forming saves over 20% of the energy used in the drying process with better water removal method and saves up to 15-25% of fibers, which leads to light-weight fiber products without the need of expensive equipment. [39] Highly porous and bulky light-weight materials could be developed into bio-based insulation of cushioning materials. The manufacturing of layered structures with excellent layer purity is also made possible by foam forming technology. [40]

In the foam forming process bubbles are mixed into a water-fiber suspension [41]. The fiber for cellulose-based foams is typically a type of wood pulp. A foaming or surface-active agent can also be added. MFC can be added for improved strength. [38]

Foam formation has been achieved mainly on laboratory and pilot scale. Further research and testing are needed before the technology can be taken to production scale. [40]

3.2.5 Screen Printing

Screen printing is a widely used method of fabrication, especially with printed electronic components. Screen printing permits the fabrication of conductive and flexible electronic products.

Printed electronics are the combination of printing processes and ink chemistry in order to manufacture electronic components [42]. This fabrication method enables technologies with properties such as high surface area, flexibility and lower costs and higher efficiencies than those of conventional technologies [43].

The screen printing process utilizes a screen mesh, through which ink is passed through by applied pressure. The non-printed area of the screen is covered by a polymer emulsion while the printed area is exposed, allowing the ink to pass through the mesh. [42]

Screen printing can be used for the deposition of layers with thickness raging from several micrometers to around 100 micrometers. Screen printing has been used to produce printed electronics applications such as solar cells, sensors and transistors. [42] Nanocellulose has in addition been used to create bioinks for printing three-dimensional porous structures [43].

Nanocellulose is a promising material for the formulation of conductive inks, but also as a substrate for printed electronics. Nanocellulose films fulfill the requirements for successful fabrication of printed electronics. These requirements are a smooth and non-porous substrate, as well as the ability to sinter the samples. Nanocellulose substrates for printed electronics applications are commonly based on MFC. [42]

In a study by Pammo et al., free-standing MFC films were fabricated as substrates for printed electronics. Graphite ink was used for the screen printing process, and it was found that the electrical conductivity of the printed patters was dependent on the roughness of the film surface. The films were found to be suitable for printed electronics. [9]

While MFC films for screen printed applications exhibit great mechanical, optical and thermal properties, as well as flexibility, pure MFC films are still expensive. However, the price of nanocellulose is believed to decrease with the growth in industrialization. [42]

3.2.6 Solvent Casting

There are two main ways of fabricating MFC-based films from aqueous dispersions. These methods are vacuum filtration and solvent casting. [23] Films formed using this method are free-standing. Solvent casting will be discussed in this chapter, while vacuum filtration will be discussed in chapter 3.2.9.

In solvent casting, the solvent evaporates, resulting in the cellulose fibrils approaching each other and increasing interactions and accumulation. The fibrils form a densely packed network, morphing into a nanocellulose film, which is then removed from water. The film is often placed under pressure in an oven to accelerate drying and avoid wrinkling. [23] Films can additionally be compression molded under heat [44].

Solvent casted nanocellulose films can also be prepared by using CNC. These CNC-based films prepared by this method were piezoelectric and biodegradable. However, plain CNC-based films from highly fluid dispersion was difficult, thus no free-standing films were obtained. [45]

Solvent casting has been used to prepare MFC-based nanopapers and bioinspired nanocomposites [23], while CNC-based films were hypothesized to replace non-degradable piezoelectric films [45]. However, as for nanopapers and nanocomposites susceptibility towards humidity may limit some real life applications [23].

One of the most significant weaknesses of the solvent casting method is its time-consumption, since solvent casting commonly requires three days for the film to dry. Additionally, wrinkling of the films is hard to avoid. [46]

3.2.7 Spin Coating

Most common layer-by-layer nanocellulose coating techniques are spin coating and dip coating. [30] Spin coating can be used to form thin films of nanocellulose coating onto substrates.

Spin coating technique is suitable for a cellulose-based substrate with smaller pore size, with the coating thickness ranging in some hundreds of nanometers, and it is a reliable method to produce reproducible and smooth thin films. The technique is based on the removal of the liquid phase from the material suspension by the utilization of high-speed spinning. [30]

First reported fabrication of ultrathin CNC films by spin coating dates back to 2003, when Edgar and Gray produced smooth films using the method and stabilized them with a mild heat treatment [29][47]. Since this report, ultrathin CNC films have largely been prepared using their method [29].

In spin coating, a cellulosic solution is deposited onto a substrate, which is then spun at a high speed. Spin coating utilizes the centrifugal force to spread the material into a film. This method has been widely used to create ultrathin cellulose films, and while there are no commercialized applications as of yet, ultrathin films have shown potential in fields like biomedicine and electronics [29].

Spin coating method results in a solid film with a high degree of reproducibility. Spin coated films made from trimethylsilyl cellulose are nearly amorphous. [29] When compared to dip coated nanocellulose films, spin coated films could be prepared as many as 80 times thinner [30]. Limitations for spin coated cellulose films, specifically MFC-based films, include susceptibility to gel formation [29]. In addition, a decrease in oxygen barrier properties in higher humidity was detected, while oxygen barrier properties had been high at a low humidity [30].

3.2.8 Spray Coating

Spray coating, more precisely thermal spray coating, is a fabrication technique where melted or heated materials are sprayed onto a surface in a stream of droplets. The spraying is then followed by flattening, rapid cooling and solidification.

As a method of nanocellulose film preparation, spraying nanocellulose has recently seen a rise in its interest. With spray coating, a very uniform deposition layer of nanocellulose can be achieved, particularly when nanocellulose is spray coated onto a polished stainless steel plate to create free-standing films. Spraying can also decrease the operating time. [28]

Spray coated films made of MFC have properties such as added smoothness, density when basis weight is raised, strength and a high number of fiber–fiber bonds, which can increase the stiffness. Compared to MFC-based films fabricated with vacuum filtration the stiffness of spray coated films was higher. [28]

Drawbacks for this nanocellulose fabrication technique seem to remain scarce. However, perhaps the most notable drawback seems to be the limited basis weight for the films, despite the easy tailoring possibilities [28][46].

3.2.9 Vacuum Filtration

In 2009, Nogi et al. fabricated nanocellulose films by dissembling the cellulose fibers' original structure. They used powdered wood as a starting material, and after removing lignin and hemicelluloses, ground it in a water-swollen condition. These processes were followed by freeze-drying and mechanical compression under a vacuum. To obtain translucent films, freeze-drying was switched to piling the nanofibers uniformly in a wet sheet and the films were polished afterwards. A wire mesh and filter papers were utilized in this experiment. [31]

Like in the 2009 study, with the vacuum filtration method films are prepared by filtering fiber suspensions using a mesh filter, where fibers gather in the form of a film [28]. The solvent is removed using an assisted vacuum [23]. This process is followed by hot pressing [33].

Vacuum filtration is a fast, simple and scalable process and often used to manufacture layered nanocellulose structures. Vacuum filtered films and membranes are densely packed, porous and the diameter of cellulose nanofibrils in them ranges between 3–5 nm. Pore size and molecular weight of membranes can in addition be controlled by using nanocellulose with varying fibril diameters. [33] Vacuum filtration leads to better mechanical properties, since it increases the orientation of the fibrils. [23]

By vacuum filtering a thin layer of CNC onto a support layer, multilayered anisotropic membranes have been fabricated. This method was followed by dip coating, a method which was discussed in chapter 3.2.2. [33] Vacuum filtration has also been used to dewater MFC to form cellulose nanopapers. These films were strong, especially films fabricated with high DP, as well as though. In addition, high porosity increased the strength of these MFC films. [12]

Another way of fabricating translucent nanocellulose films is by TEMPO-mediated oxidation. This method was achieved by Fukuzumi et al. in 2009, when the research team oxidized softwood and hardwood celluloses with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). After removing unfibrillated and partly unfibrillated fibers, the recovered gel was converted into films using vacuum filtration. In addition to the high crystallinity, the tensile strength and stiffness of these films were much higher than that of cellophane films. The hydrophilicity of these films is also easily adaptable by a simple soaking treatment. [8] In other studies of MFC-based TEMPO films, it has been found that vacuum filtration and moderate hot pressing leads to increase in strength and elongation of the films. [23]

While vacuum filtering is a common method of fabricating nanocellulose films, some limitations still remain. For example the filtration time increases exponentially with film thickness and vacuum filtered films have issues when separating the film from the filter [46].

3.3 Usages of Film Technology

The use of film technology spans from industrial use to everyday applications. Depending on the material and the fabrication method of the film, different properties can be passed onto the film, including wear resistance, electrical conductivity, biocompatibility, optical properties, resistivity and so on [6][13][25][27].

Thin-films can be used in applications such as coatings, packagings, consumer electronics, sensors, medical devices and diagnostics. The application possibilities are innumerable.

Thick-film technology is used for electronics and sensor manufacturing, especially in the automotive industry. Thick-films are able to stand high electric power and severe environmental conditions, which makes them more usable for more demanding applications than thin-films.

Film technology is a vast field of multiple disciplinaries that utilizes many different techniques and materials. Nanocellulose films are but a branch of this field. The applications and possibilities of nanocellulose films will be discussed in greater detail in chapter 4.4.

4. NANOCELLULOSE FILMS

Nanocellulose films combine the properties of nanocellulose and film technology. Nanocellulose-based films have the potential to be used in new application areas, and the need for fundamental and applied research is urgent [7]. In addition to coatings and intermediate layers, these nanocellulose-based films have been found to be light-weighted, renewable, recyclable, processable and biocompatible [6].

The optical, mechanical and thermal properties and potential use in electronics of films made with pure MFC was first reported in 2009 by Nogi et al. [7][31]. The smooth surface of nanocellulose films enable the attachment of printed electronics and the density of it provides excellent oxygen barrier properties [26][48]. The potential applications of nanocellulose films are numerous [26].

The properties and application areas of nanocellulose-based films will be discussed in the following sections. Different fabrication methods and their advantages and limitations will in addition be discussed.

4.1 Properties of Nanocellulose Films

As discussed in chapter 2.4, nanocellulose's properties differ from those of traditional cellulose because of its higher surface area and increased interactions. Nanocellulose has many interesting properties, such as high crystallinity, non-toxicity, conductivity, strength and so on.

In a film, nanocellulose fibers are usually long in length, interlocked and densely packed. It has been found that nanocellulose films, specifically those made out of MFC, give the potential to achieve high density in cross-linked structures. This leads to low porosity and high resistance to air permeation. [6]

In addition, nanocellulose-based films demonstrate enhanced intrinsic characteristics, such as optical, mechanical, thermal and insulating properties, and multiple functions, such as fire-retardant, magnetic or electric properties [7]. Unusually high straining ability has also been demonstrated, as well as a large difference in properties of multilayer films, depending on the order of layer deposition. Electrically conductive nanocellulose films have been prepared by incorporating tin-doped indium oxide, carbon nanotubes and silver nanowires into a multilayer structure. [6]

Oxygen barrier properties, as well as the possibility to chemically modify nanocellulose films for different properties, open doors for interesting application areas [28]. These areas and future possibilities will be discussed in the next chapter.

4.2 Applications and Possibilities

The first films made of cellulose were manufactured in 1898 from viscose. These films were prepared by Charles Frederick Cross, Edward John Bevan and Clayton Beadle. Commercial production of thin, transparent cellulose films, developed by Dr. Jacques Brandenberger, begun in 1913 in France. [44]

Since then, with the growing interest towards sustainable and renewable materials, cellulose-based films in different application areas have garnered popularity. Nanocellulose has been studied as a replacement for synthetic polymers, for example as packaging materials. There is a widespread desire to replace petroleum-based materials with life-friendly nature-based materials, and the information on the performance of nanocellulose-based packagings is accumulating quickly [6].

Nanocellulose films have been shown to demonstrate enhanced intrinsic characteristics and multiple functions. This extends the application possibilities of nanocellulose films from traditional fields to emerging high-tech fields, such as electronic and photonic devices, clean energy, biomedicine, sensing and the environment. [7]

Printed electronics, sensors, biosensors, flexible displays and diagnostic devices are examples of cellulose-based applications in electronics. Because of the high smoothness of most nanocellulose-based substrates, the surface is optimal for printing high quality, conductive electronics. With the screen printing method, nanocellulose-based applications such as flexible displays, solar cells, electrodes and transistors are possible to produce [29][42].

In the biomedical field, applications concerning controlled drug release, tissue engineering, sensor technology and cell culturing are interesting topics. MFC-based films have successfully been used in controlled drug release [49], and as filter papers for virus removal [50]. BNC, which is highly pure and biocompatible, has been used to produce vascular grafts. It has also been proposed as a material for wound dressings. [12] Cellulose-based thin-films have also shown potential in the detection of biomolecules, such as DNA or proteins, which could be commercialized for enzyme immobilization and antibody reaction [29].

In a 2017 study, cell alignment on MFC surfaces was achieved, as well as cell cultivation directly on charged MFC surfaces. Cell alignment is a favorable not only in biomedical applications, but also in composites in improving stiffness and strength of the structure. [51] Nanocellulose-based materials have been studied to be used as reinforcing agents in nanocomposites. With foam forming, bio-based insulation and cushioning materials are in addition achievable.

Because of the good oxygen-barrier properties of many cellulose-based films, as well as their non-toxicity, application possibilities such as future food packaging materials have also been proposed. Because of the bioadsorbency of nanocellulose, the material has shown promise in water treatment and purification. Nanocellulose could be used to remove viral and heavy metal particles from aqueous solutions. [7][33]

Sensor technology is also an emerging nanocellulose-based technology. Utilizing different nanocellulose materials, fabrication methods and added elements can produce sensor technology including piezoelectric, strain, humidity, photoelectrical and biosignal sensors, just to name a few [20][29][42][43].

While the application areas are vast and research on nanocellulose-based applications is rapidly being conducted, the actual real life application possibilities are in some cases still in the future. Nanocellulose films have potential uses in many different areas, but reproducible preparing of films at laboratory and industrial scale is still slow, often because of time-consuming film fabrication methods [46]. Issues with processing, high-cost materials and fabrication methods are slowing the progress of nanocellulose-based technology, although the common consensus seems to be that prices are expected to drop as the industry continues to grow.

4.3 Stability and Challenges

The different fabrication methods for nanocellulose films and the properties of said films will be discussed in this chapter. For certain applications, certain fabrication processes are more appropriate than others. The advantages and limitations of different processes will be presented and compared.

The results of this comparison are gathered into Table 1. In the table, the most relevant nanocellulose type(s) for the fabrication method, either microfibrillated cellulose (MFC), cellulose nanocrystals (CNC) or bacterial nanocellulose (BNC), which were discussed in chapter 2.4, is presented. The film type, either a coating or a free-standing film, is presented, as well as the advantages and limitations of the films manufactured by the fabrication method. Some examples of application areas for these film fabrication methods are also mentioned.

Table 1. Comparison of different fabrication methods.

Fabrication method	Nano-cellu-lose type	Film type	Advantages	Limitations	Applications
Biofabrication	BNC	free-standing	-high purity -high crystallinity -tailorable properties -piezoelectricity -good biocompatibility	-slow fabrication process -tight pore structure	-vascular grafts -sensors -food packaging materials
Dip Coating	MFC	coating	-anisotropic coatings -small pore size	-delamination due to small pore size -sensitivity to humidity	-biobased packaging materials
Electrospinning	MFC, CNC	free-standing	-porous films -high surface area -conductivity	-solvents require specific conditions -not feasible for continuous production	-sensor materials -ultrathin fibers
Foam Forming	MFC	free-standing	-cheap to manufacture -need for less materials -high surface area -highly porous -excellent layer purity in multilayered films	-this method is largely still in development	-packaging materials -insulation -wastewater treatment -paper deinking
Screen Printing	MFC	coating	-ability to produce printed electronics -conducting patterns -high surface area -cheap to manufacture	-MFC is still expensive	-printed electronics -bioinks -sensor materials -solar cells
Solvent Casting	CNC, MFC	free-standing	-densely packed films -piezoelectricity -widely known and used method	-plain CNC films from highly fluid dispersion is difficult, no free-standing films were obtained -susceptibility towards humidity -slow -wrinkling	-nanopaper -bioinspired nanocomposites
Spin Coating	CNC, MFC	coating	-very thin films -oxygen barrier properties -small pore size -reproducible -smooth films	-susceptibility to gel formation -sensitivity to humidity	-biobased packaging materials
Spray Coating	MFC	coating, free-standing	-ability to manufacture free-standing films when cellulose is sprayed onto stainless steel plate -quick -flexible films	-limited basis weight	-sensor materials -biomedical scaffolds
Vacuum Filtration	CNC, MFC	free-standing	-tailorable properties -strength -toughness -densely packed films -quicker than solvent casting	-long filtration time when fabricating thicker films -problems in separating the film from the filter	-sensor materials

From the table, we can see that different fabrication methods produce films with varying thicknesses, properties and application possibilities. Depending on the application area, differently manufactured films exhibit properties that are advantageous, while others exhibiting same properties may be considered disadvantageous. For instance, porosity and thickness are largely application specific properties.

Advantages not included in the table, such as non-toxicity, renewability and eco-friendliness, are applicable to all of these methods. As for limitations, it can be stated that most nanocellulose materials still remain expensive, which hinders all industrial scale production of nanocellulose-based films. This is largely because of the relative youth of the industry.

Most nanocellulose-based films exhibit properties like denseness, strength and good oxygen barrier properties. Likewise, limitations often include sensitivity to humidity or wrinkling. Some nanocellulose materials have issues with breakage, thermal degradation and alignment of nanocellulose [6].

Issues regarding nanocellulose film fabrication can be overcome with research and new innovative methods of fabrication. Traditional methods, such as solvent casting and vacuum filtration are time-consuming methods because of long drying times and sensitivity to wrinkling. Methods to optimize drying, such as the film-drying setup for MFC films presented in the study by Pammo et al., where a plastic cone was placed over the film and heated [9], or a rapid fabrication method by Shanmugam et al., where cellulose is sprayed onto a surface [46], are needed for more effective production.

Fortunately, new methods and approaches to improve properties of nanocellulose, such as studies focused on improving the relatively poor humidity resistance of nanocellulose-based films [52], are being conducted as we speak.

5. CONCLUSION

As the most abundant natural polymer on earth, cellulose has garnered much attention over the years, often from the point of view of materials science. While cellulose-rich materials like wood and cotton have been used by humans for some millenniums, nanocellulose-based materials have only gained fame fairly recently.

Because of the relative youth of the industry, issues with high-cost materials and fabrication methods somewhat hinder the progress. However, with properties that offer solutions to many of the currently hot topics regarding the environment, such as sustainability, renewability, recyclability and non-toxicity, nanocellulose is a material of possibilities in many regards. Added unique properties concerning its crystallinity, porosity, mechanical, optical and chemical properties, as well as the ability to tailor these properties according to need with some applications, it is no wonder that nanocellulose has gained the interest of a broader audience in recent years.

The properties of cellulose and nanocellulose, common nanocellulose film fabrication methods and applications, as well as the typical usages of cellulose and film technology have been introduced and discussed in this paper. The purpose of this paper was to study nanocellulose as an efficient material for film fabrication, as well as compare and evaluate different fabrication methods.

Given how different fabrication methods work better for some film types than others, it is impossible to choose the most efficient method of film manufacturing. However, when the goals and constraints of the project are known, fabrication methods can be compared and evaluated based on how they fit the criteria. For example, some spraying methods are considerably faster than traditional solvent casting but might lack in the ability to produce other desired properties, such as correct density or electric properties.

All in all, it can be stated that nanocellulose offers many possibilities for the future of film technology. Depending on the type of nanocellulose, as well as the processing and fabrication methods, nanocellulose films can be applied to a vast category of fields. Application possibilities ranging from water purification, packaging materials, and insulation to the medical field, tissue engineering and electronic engineering field offer new possibilities and challenges. Given time and recourses, the application areas are innumerable.

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